SYMPOSIUM ON FUEL CELLS
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ION-EXCHANGE MEMBRANES IN HYDROGEN-OXYGEN FUEL CELLS

By

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1. GENERAL

In fuel cell technology, simplicity of form and construction are desired engineering features. In conventional fuel cell systems for instance, electrodes must have uniform porosity to insure an even distribution of gas. Construction flaws and other imperfections cause gas accumulation in the electrolyte and mixing of gases when slight gas pressure difference occurs. In addition sintered metal electrodes are fragile and porous carbon electrodes are both fragile and bulky. The production of these items, in addition, is time consuming and almost amounts to a custom manufacturing operation. It is because of these drawbacks, that the ion membrane fuel cell has attracted so much attention. Essentially it consists of an ion-exchange membrane, cationic or anionic in form, and two "catalytic" electrodes held against each side of the membrane. Reactant gases are brought to either side of the membrane, electron exchange occurs at the catalyst-membrane interface and current flows. The positive advantages of the ion-membrane cell are:

(1) Electrolyte remains non-diluted by water formed as a result of reaction.
(2) The membrane serves as a gas impervious barrier.
(3) The cell is relatively insensitive to gas pressure variation which would cause gas accumulation in the electrolyte of an ordinary liquid electrolyte fuel cell.
(4) Electrode flooding is minimized.

In practice the ion-membrane fuel cell has fallen far short of the expectations and indeed none, to the best of our knowledge, has ever been able to sustain satisfactory power level for a reasonable length of time, e.g., 0.5 - 0.6 volts at 30 - 40 milliampere per square centimeter for three to six months.

A reflection of these operating difficulties can be obtained by comparing the performance of an ion-membrane fuel cell operating on pure hydrogen and oxygen and incorporating platinum catalysts on graphite cloth electrodes in an ionics Fuelox type fuel cell. The comparison is illustrated in Figure 1 and indicates that polarization occurs much more rapidly than for the "non-dry" fuel cell.

2. SOME FACTORS RELATED TO EFFICIENT ION-MEMBRANE FUEL CELL PERFORMANCE

An examination of polarization curves and other data indicate that the hydrogen-oxygen ion-membrane cell has some serious disadvantages which must be overcome in order to attain satisfactory operating conditions. Some of these are:

A. Cell polarization resistance.
B. Drying of membranes.
C. Carbonate formation from carbon containing fuels.

A. Membrane Resistance

The ion exchange membrane is used as the electrolyte component in the fuel cell and while having structural advantages inherent in a solid material it does suffer from the disadvantage that the ionic conduction of leached hydroxyl form anion membrane will be roughly about 1/20 that of a comparable volume of concentrated KOH. 6N KOH in a layer the thickness of our membrane (0.06 cm) has a resistance of .11 ohm-cm^2. Thus the membrane resistance will be one or two ohm-cm^2.

FIGURE 1

HYDROGEN-OXYGEN FUEL CELL
COMPARED WITH FUELOX CELL

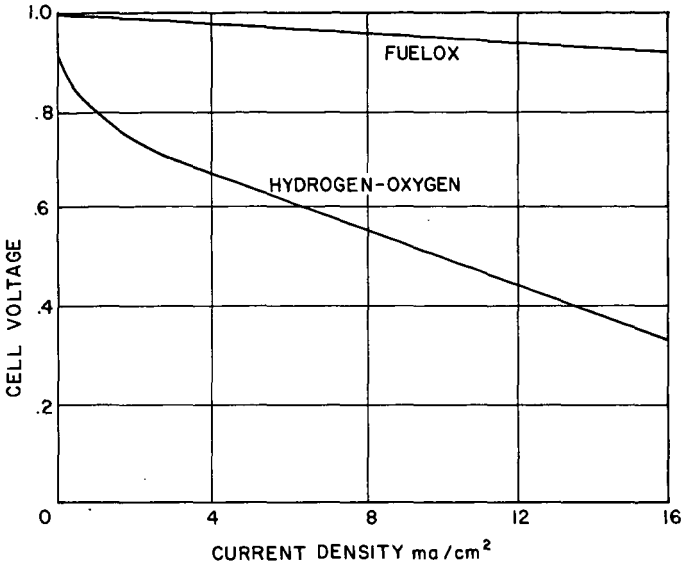
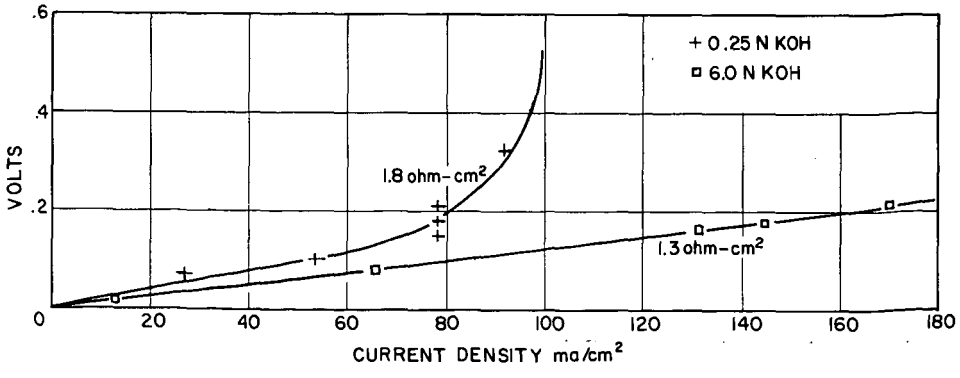


FIGURE 2

MEMBRANE RESISTANCE

ANION MEMBRANE COMPLETELY IMMERSED IN KOH
DIRECT CURRENT



The result of the resistance characteristics of such membranes as well as electrode and concentration polarizations is shown in Figure 1. The hydrogen-oxygen cell is constructed with an anion membrane that was equilibrated in 6N KOH. The slope of the linear position of the curve is 34 ohm-cm^2. One of the objectives of our study was the determination of the source of this high voltage loss, since the membrane resistance alone obviously cannot account for the observed drop.

We first measured the membrane resistance. An investigation of membrane resistance calls for reliable technique under operating conditions approximating those found in actual performance. In routine work membrane resistance is essentially determined by placing platinum tipped probes on either side of a membrane and utilizing a Wheatstone Bridge circuit to determine the desired membrane resistance. Results, although reliable for industrial type uses are semi-quantitative and are not obtained under operating conditions comparable to those found in fuel cells, i.e., alternating current is used. The technique used consists of placing the membrane vertically in KOH (for the anion type) or HCl (for the cation type). Calomel electrodes with capillary salt bridges were placed on opposite sides of the membrane with the tips of the salt bridges touching the membrane. A current was passed through the solution by means of a battery and platinum electrodes placed well away from the membrane. The voltage differential between the calomel electrodes was measured with a Beckman Model G millivoltmeter as a function of current. Figure 2 shows the results of an anion membrane in 0.25N KOH and 6N KOH. The resistance of the former is about 2 ohm-cm^2 and the latter 1.3 ohm-cm^2. It may be noted that in the dilute solution a rapid voltage rise occurs at 90 ma/cm^2. This will be commented on later.

In an effort to separate the hydrogen and oxygen electrode polarizations, half cell studies were undertaken. In this technique (Figure 3) a gas electrode is placed on one side of the membrane while solution is on the other side. A salt bridge-calomel cell is placed against the membrane on the solution side. A current is driven with a battery between the gas electrode and a platinum electrode in the solution. The voltage between the gas electrode and the calomel is measured.

Figure 4 shows the results of hydrogen generation and hydrogen utilization with an anion membrane and 6N KOH solution. The former gives a voltage loss equivalent to 6.1 ohm-cm^2 and the latter 7.7 ohm-cm^2. The difference may be due to hydrogen concentration polarization.

Figure 5 shows the same experiments except that oxygen evolution and utilization are carried out. The irreversible voltage loss usually ascribed to a peroxide decomposition mechanism is apparent. In addition a pronounced voltage drop at low current densities is also observed in agreement with other workers.

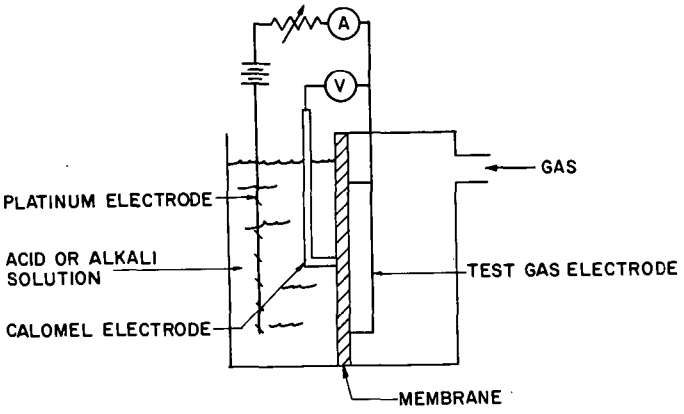
Another technique was also used to study the hydrogen electrode. In principle, the technique involves imposing a potential across a membrane supported between two hydrogen electrodes one of which utilizes hydrogen and the other of which generates hydrogen. Both chambers are filled with hydrogen at atmospheric pressure and a battery is used to drive the reaction. A diagram of the experimental approaches is shown in Figure 6. Since the hydrogen electrode is fairly reversible one could examine different hydrogen electrodes (utilizing hydrogen) with a standard electrode evolving hydrogen. Figure 7 illustrates the result of such an experiment using an anion membrane equilibrated in 6N KOH. The slope indicates a total loss of 52 ohm-cm^2. At this point we humidified the hydrogen gas going into each compartment by bubbling the gas through water at 70°C. and excess gas was passed through the cells. The voltage-current density curve changes appreciably down to 16 ohm-cm^2. It may be noted that the two half cells with hydrogen utilization and hydrogen evolution gave 7.7 and 6 ohm-cm^2, respectively, so that the humidified hydrogen-hydrogen dry cell approximates quite well the sum of two half cells.

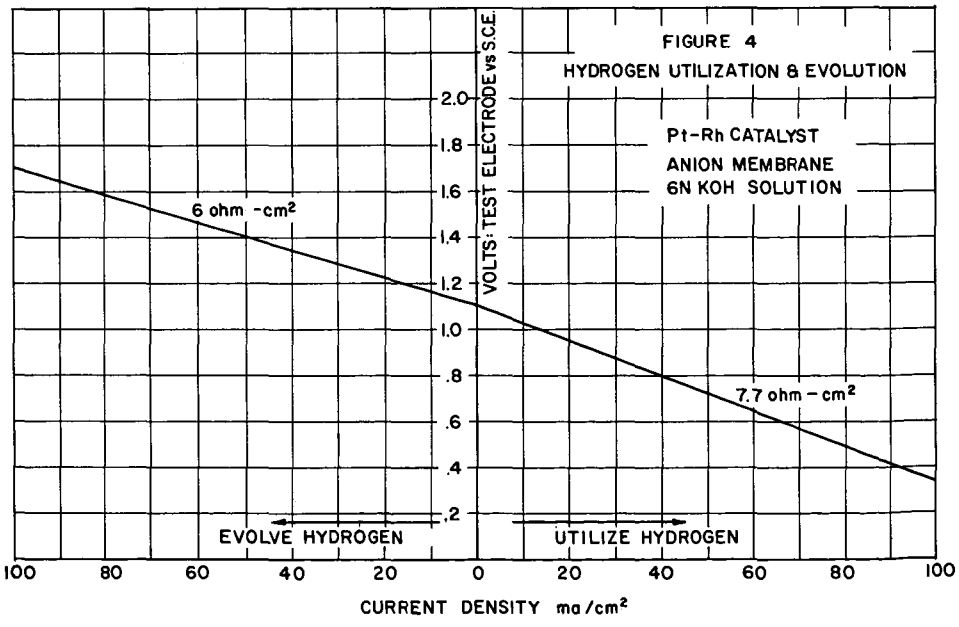
B. Dehydration

The original hydrogen-oxygen cell yielded a 34 ohm-cm^2 slope as mentioned in the beginning of the paper.

This cell was operated again, but with humidification. Figure 8 illustrates the voltage-current density curves of hydrogen and oxygen half cells, the difference between them, and the actual humidified hydrogen-oxygen cell. The latter has a slope of 22 ohm-cm^2 and is quite close to that predicated with the half cells. From these data it is seen that drying in the vicinity of the electrode area increases greatly the contact resistance at the membrane catalyst interface. Membranes are approximately

FIGURE 3
HALF-CELL TEST EQUIPMENT





60% water and it can be seen that variations in water content at such surface areas could result in significant changes in ion diffusion rates and more importantly, conductivity of the desiccated portions. Desiccation in all liklihood occurs as a result of the relatively dry fuel gases increasing the rate of evaporation from the surface of the membranes. A number of mechanical arrangements for providing rehumidification have been attempted but it has been found that such approaches are merely stop gas measures which at higher current densities fail to provide solutions to the drying problem.

Ionics has experimented with more "intrinsic" solutions to the problem; one of them mentioned earlier in the paper is the use of semi-dry cell such as the Fuelox cell where the cathode compartment contains aqueous solution of reactants and thereby keeps the cation membrane sufficiently moist even at current densities as high as 50 amp/ft^2. Cells of this type have run for 1000 hours on half hour charge-discharge cycles at about 20 ma/cm^2.

Another approach to this problem involves the "dual membrane" concept (1) which not only eliminates the humidification problem but decreases the conductivity of the membrane components of the fuel cell assembly.

C. Carbonate Formation

In the last analysis the efficient and economical use of the ion membrane fuel cell will rest heavily on the performance of carbonate producing fuels in such power producing devices. Because of its importance it was deemed advisable to determine the effect of carbonate production on the operating characteristics and performance of an ion-membrane cell. A fuel cell using carbon monoxide and oxygen as fuels and a 6 mm thick anion membrane with two waterproofed platinum on graphite electrodes was tested. Figure 9 depicts the performance of this cell. The recorded open circuit voltage is 0.80 - 0.86 volts. After operating for eleven hours the cell was taken apart. The electrode and membrane were found to contain a considerable quantity of solid carbonate.

Alternate tests with membranes soaked in acid were comparatively poor. The maximum open circuit voltage 0.37, the maximum current being about 1 ma/cm^2 at 0.2 volts for a short time.

3. DISCUSSION

1. High Cell Resistances

These resistances are the limiting factor in obtaining high current densities in ion-membrane fuel cells. Possible solution to these problems lies primarily in the area of improved catalyst membrane contact.

2. Drying Out of Membranes

This is a most serious engineering problem and can be solved by:

(a) Using a membrane where desiccation problems are not as serious due to low water content. This will also tend to avoid the rapid se in voltage which was observed to occur when membrane resistances were measured in 0.25N KOH. Thus during cell operation a salt concentration gradient forms in the free water phase in the membrane, as well as in any free water between the catalyst and the membrane. With low water content membranes these gradients should be minimized.

(b) Mechanical "wicking" arrangements have been used, but have not provided a satisfactory means for attaining high current density. Of course, humidification of the fuel gases is a possibility but does involve increased weight and cost penalties.

(c) The best technique found to date is essentially the constant humidification of the membrane as mentioned previously in the Fuelox type cell or the dual membrane cell. An added advantage of this system is that water of formation due to hydrogen-oxygen reaction can be removed by use of dry gases and thereby does not cause undue dilution of the electrolyte being used.

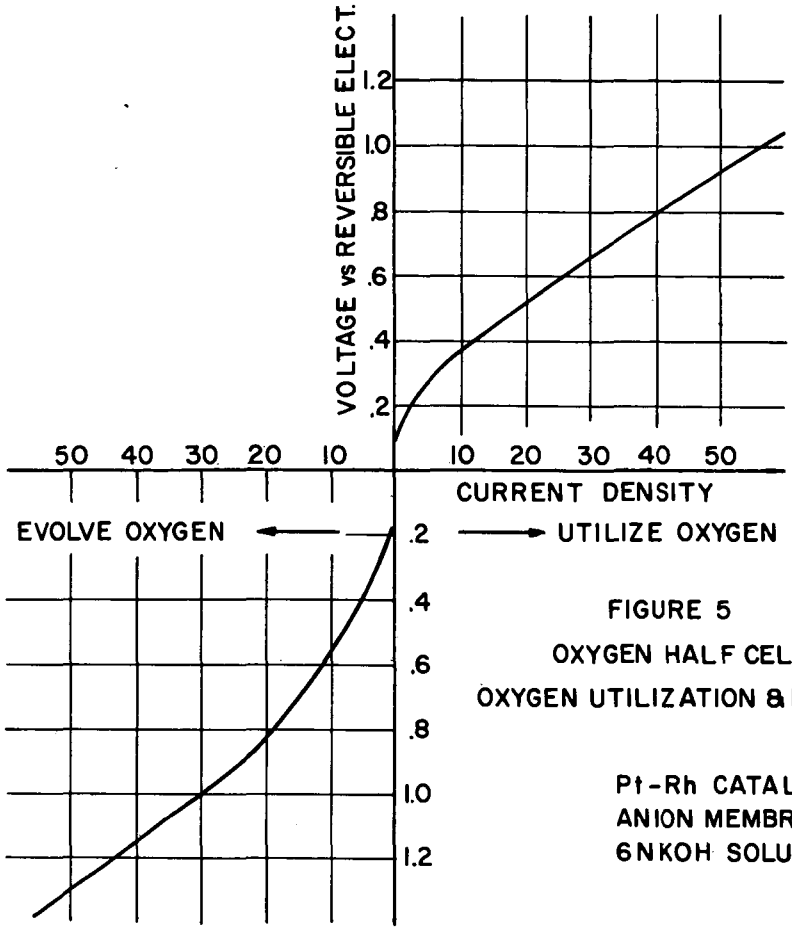


FIGURE 5

OXYGEN HALF CELL

OXYGEN UTILIZATION & EVOLUTION

Pt-Rh CATALYST
ANION MEMBRANE
6 N KOH SOLUTION

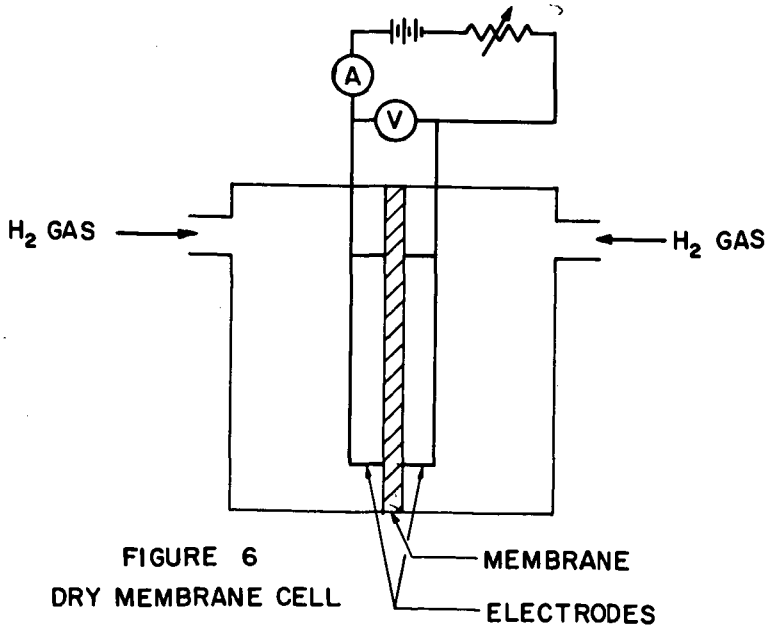


FIGURE 6

DRY MEMBRANE CELL

3. Carbonate Formation

Finally, the problem of carbonate formation remains a serious one. The data on the use of carbon monoxide as a fuel gas indicate, substantially, that the formation of carbonate at the electrode membrane interface essentially degrades operation within a short period of time. Some approaches worthy of mention for avoiding this problem are:

(a) Use of acid type membranes with subsequent venting of carbon dioxide. This, of course, has the formidable barrier of a satisfactory operation of fuel electrode in acid solution.

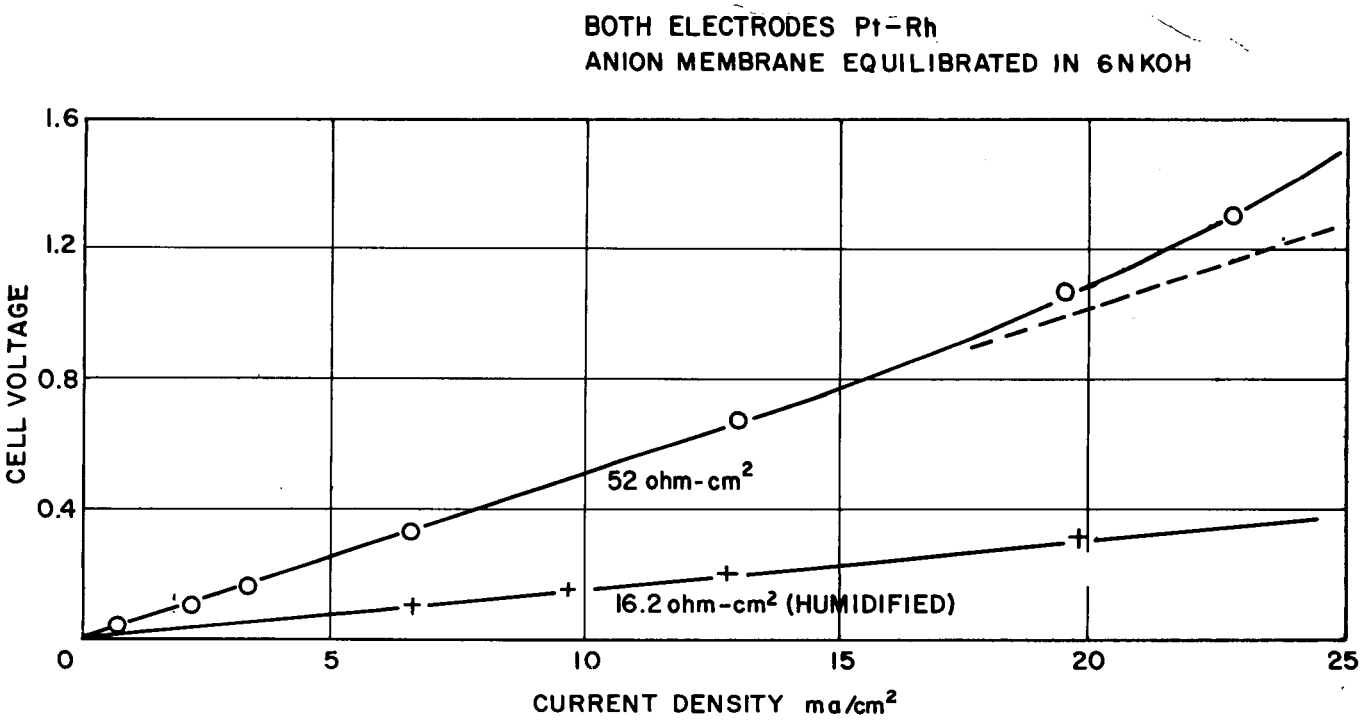
(b) Continuous regeneration techniques for membranes, i.e., the continuous removal of $CO_3^=$ ion from the reaction interface may be effected by driving the cell in reverse and moving the carbonate ions electrically away from the carbon monoxide electrode.

LITERATURE CITED

(1) Juda, W., Tirrell, C. E., and Lurie, R. M., "Fuel Cells with Ion Exchange Membranes", Energy Conversion for Space Power, Academic Press, New York (1961).

FIGURE 7
MEMBRANE CELL

HYDROGEN UTILIZATION / HYDROGEN EVOLUTION



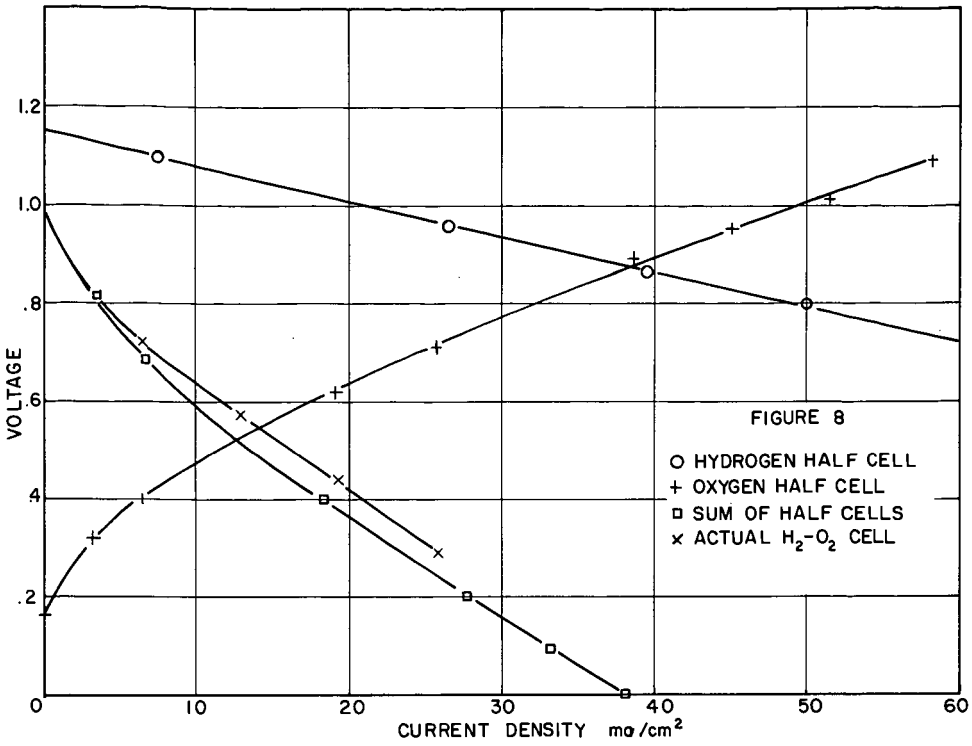


FIGURE 9

$CO-O_2$ DRY CELL

BOTH ELECTRODES – Pt ON GRAPHITE
ANION MEMBRANE – EQUILIBRATED IN 6N KOH